THE DIELECTRIC DISPERSION OF A FEW NATURAL RESINS IN NON-POLAR SOLVENTS

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ABSTRACT. The dielectric dispersion of a few natural resins in non-polar solvents has been studied. The resins include pure lac resin, soft lac resin, dammar and mastic. The critical frequency and the relaxation time of these resins have been calculated and the results confirm the comparative values of the dimensions of their rotating polar units obtained previously.

INTRODUCTION

In a previous paper (Bhattacharya, 1944 *a*) it was pointed out that dilute solutions of natural resins in non-polar solvents might yield interesting results regarding dielectric properties since the molecules of these resins would be free to move about uninfluenced by intermolecular forces. The study of anomalous dispersion of such solutions may also provide means of determining the size of ultimate particles of these resins on a comparative basis. It has already been observed (Bhattacharya, 1944 *a*, *b*, *c*) that such a dielectric study of a resin as such has helped to obtain fruitful and interesting results in some cases. On account of the polar nature of most of the natural resins as well as their large and complex molecules the dielectric dispersion method of study of their solutions in non-polar solvents is expected to be of material help in elucidating the inner structure of these macroscopic molecules.

The present study concerns only three natural resins in non-polar solvents, *viz.*, dammar and mastic in benzene and lac in dioxane. Lac as such has not been used but its two main constituents, pure lac resin (reinharz or α-lac) and soft lac resin, have been used separately in dioxane solutions for reasons already stated (Bhattacharya, 1943). We have arrived at some conclusions regarding the particle size of these resins from their behaviour in the alternating electric field. The study of their solutions now provides means of testing those results from another point of view, since inner friction of these resins is greatly reduced in these solutions.

THEORETICAL

Williams and Oncley (1931) have extended Debye's dipole theory to the binary system in which a non-polar solvent is used as regards the variation of dielectric constant and dielectric loss with frequency. They have shown that Debye's original equations (1929) for polar liquids under the influence of high frequencies may be applied to such binary systems. Thus they obtain the following equations,

$$\epsilon'_{12}=\epsilon^{\infty}_{12}+\frac{\epsilon^{0}_{12}-\epsilon^{\infty}_{12}}{1+x^2} \qquad \ldots \quad (1)$$

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$$\epsilon''_{12} = (\epsilon^0_{12} - \epsilon^\infty_{12}) \frac{x}{1+x^2} \qquad \ldots \quad (2)$$

where $$x = \frac{\epsilon^0_{12}+2}{\epsilon^\infty_{12}+2}\omega\tau = \frac{\epsilon^0_{12}+2}{\epsilon^\infty_{12}+2} \cdot 2\pi f\tau$$

ϵ'_{12} = dielectric constant of solution at frequency f,

ϵ''_{12} = dielectric loss of solution at frequency f,

ϵ^∞_{12} = dielectric constant of solution at very high frequencies,

ϵ^0_{12} = dielectric constant of solution at low frequencies,

and τ = relaxation time of solute.

The ϵ^∞_{12} value is usually obtained from refractive index measurement from the relation

$$\epsilon^\infty_{12} = n^2_{12}$$

The dielectric loss attains the maximum value at a frequency f_c which is called the critical frequency and is given by the relation

$$2\pi f\tau = 1 \qquad \ldots \quad (3)$$

Thus from (1), (2) and (3) the relaxation time τ and the critical frequency f_c of the solute particles may be calculated when ϵ'_{12}, ϵ^∞_{12} and ϵ^0_{12} are known.

EXPERIMENTAL

Apparatus.—The substitution bridge method was used for the measurement of capacity. The frequency range employed was from 1 Kc/s to 2 Mc/s. The bridge was the high frequency type 516-C of General Radio Co. The detector was a pair of high-sensitivity headphones used in conjunction with a high-gain wide-band amplifier designed by Dr. H. Rakshit, of the University College of Science and Technology, Calcutta. The oscillator was the General Radio-modulated oscillator type 684-A. The condenser could be set to an accuracy of better than 0·05 $\mu\mu$ F.

The experimental cell was constructed of pyrex glass according to the design of Sayce and Briscoe (1925). The silvering was done according to the directions given by Sugden (1933). This cell could be placed inside a big thermo-flask. The temperature of water in this flask could be maintained constant to 25° ± ·05C and thus it served as a good thermostat. The thermo-flask water was earthed. Screened cables were used for connecting the bridge with the oscillator and the amplifier.

MATERIALS

Benzene.—The method of purification of the sample of benzene used has already been described (Bhattacharya, 1942). Its constants agreed well with the standard data and are as follows:—

F.P. = 5.5°C, $n^{25} = 1.4.985$, $d^{25} = 0.8738$, $\epsilon^{25} = 2.2725$

Dioxane.—The sample used was American produce bottled by A. Boake Roberts & Co., Ltd., of England. This was purified according to the method described earlier in another paper (Bhattacharya, 1942). The constants of this sample are as follows:—

$$F.P. = 11.6°C,\ n^{25} = 1.4198,\ d^{25} = 1.0282,\ \epsilon^{25} = 2.2024.$$

Dammar.—The sample of dammar was obtained from Napier Paint Works, Ltd., Calcutta, and was very pale yellow in colour. It was melted and filtered through two folds of muslin cloth in order to free it from dirt and woody matter which might have been present. It was remelted and the scum that formed on the top was removed. The clear liquid at the bottom was allowed to solidify. This resin, when cold, was powdered to pass through a 80 mesh sieve and desiccated under vaccum. Its constants are :

Acid value 39·5, softening range 100°-104°C, melting range 112°-117°C.

Mastic.—The mastic resin was also obtained from Napier Paint Works, Ltd., Calcutta, and was in the form of rounded pale yellow granules. It was subjected to the same method of purification as dammar resin. The constants of this are as follows :

Acid value 58·5, softening range 70°-72°C, melting range 78-85°C.

Pure lac resin.—The sample used was the same as had previously been utilised for the determination of its electric moment. The method of purification was fully described in that earlier paper (Bhattacharya, 1943).

Soft lac resin.—This was also the same sample which previously had been used for the measurement of its dipole moment. For details of the method of purification, etc., the previous paper (Bhattacharya, 1943) may be referred to.

METHOD OF PROCEDURE

All solutions were made by weight in glass-stoppered Erlenmeyer flasks. When a resin was completely dissolved in the solvent, the solution was quickly filtered through a Jena fritted glass filter No. 11G2 under reduced pressure and closed volume. This solution was then put into the experimental cell. The measurement of capacity was done only when the cell attained the temperature of the thermostat. The power-factor knob of the bridge was adjusted from time to time in order to obtain the best condition of silence in the headphones due to conductivity of solutions.

CALCULATION

The apparatus was calibrated with pure and dry benzene taking its dielectric constant as 2·2725 at 25°C. The 'Zero-capacity' of the cell was obtained very carefully from the relation

$$C_0 = \frac{C_A\,\epsilon_B - C}{\epsilon_B - 1}$$

where C_0 = Zero capacity of the cell,
C_A = air capacity of the same,
C_B = capacity of the cell filled with benzene,
and ϵ_B = dielectric constant of benzene.

For any resin solution the dielectric constant was then determined from the relation

$$\epsilon'_{12} = \frac{C_S - C_0}{C_A - C_0}$$

RESULTS

The results obtained have been shown in Tables I and II.

TABLE I

Dielectric constant data

f.	Dammar in benzene (9·45% soln.)	Mastic in benzene. (8·15% soln.)	Pure lac in dioxane. (5·98% soln.)	Soft lac in dioxane. (9·28% soln.)
1·0 Kc/s	2·443	2·475	2·669	2·503
10 Kc/s	2·443	2·475	2·669	2·503
25 Kc/s	2·442	2·475	2·669	2·503
50 Kc/s	2·443	2·473	2·669	2·503
100 Kc/s	2·443	2·473	2·668	2·503
500 Kc/s	2·443	2·470	2·669	2·502
1·0 Mc/s	2·440	2·461	2·668	2·500
1·5 Mc/s	2·430	2·436	2·659	2·456
2·0 Mc/s	2·425	2·433	2·654	2·492

TABLE II

Solution	n_{12}	ϵ_{12}^{∞}	ϵ'	τ	f_c
Pure lac	1.4236	2.027	2.654	1.062×10^{-8} sec.	15.0 Mc/s
Soft lac	1.4270	2.036	2.492	1.108×10^{-8} sec.	14.4 Mc/s
Dammar	1.5006	2.252	2.425	2.458×10^{-8} sec.	6.5 Mc/s
Mastic	1.5002	2.251	2.433	3.634×10^{-8} sec.	4.4 Mc/s

DISCUSSION

The results have been shown graphically in Fig. 1, where it may be noticed that anomalous dispersion starts for most cases after 1 megacycles per second. In the case of mastic it starts a little earlier. Unfortunately measurements could not be pursued at frequencies beyond 2 megacycles per second with the present equipment, since it was apprehended that error of measurement would increase with the bridge used beyond this limit. For higher frequencies a heterodyne beat unit is usually employed for the measurement of dielectric constant but such an apparatus could not be built owing to the difficulty of obtaining supplies of necessary equipment due to the international situation. The experimental results obtained with the present equipment, however, are interesting and useful for the calculation of relaxation times of solutes and their critical frequency.

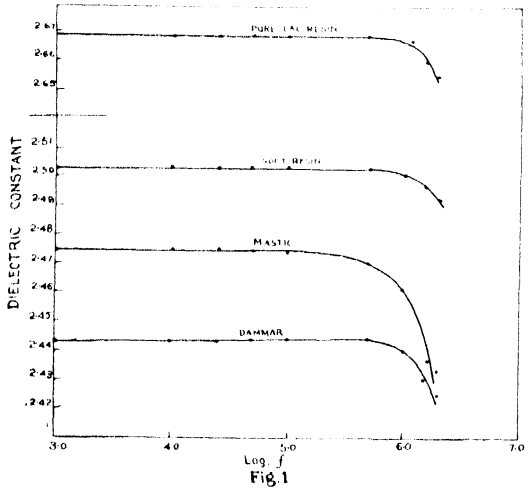

Fig. 1

Dammar and mastic resins were dissolved in benzene but the constituents of lac resin, being insoluble in hydrocarbon solvents, were dissolved in dioxane in which they are soluble and which is also a non-polar solvent. No variation of dielectric constant of either benzene or dioxane could be noticed over the range of frequency used in this investigation. Very dilute solutions were not employed owing to the difficulty of measuring very small changes in the dielectric constant values, but since these resins are comparatively high-molecular-weight bodies the molar concentrations of the resins in the solutions used for these experiments were not high. It was also noticed that indices of refraction of very dilute solutions differed little from those of their respective solvents. This is another reason why more concentrated solutions were used.

Refractive index measurements were made with a Zeiss-Abbe refractometer. The instrument was tested for the correctness and reproducibility of its readings with distilled water, carbon disulphide, benzene and dioxane. The results of measurement on resin solutions have been included in Table II along with the calculated values of relaxation times and critical frequencies. These were calculated using dielectric constant values at 2 megacycles per second for ϵ'_{12} in each case. The respective curves in figure 1 are in agreement with the critical frequency obtained for each resin.

It may be observed from Table II that the relaxation times of pure lac resin and soft lac resin rotating units are practically the same, giving thereby almost the same critical frequency for both. If we consider these solutions dilute for all

practical purposes *i.e.*, if the resin molecules are considered to be free from any interaction among themselves, their inner friction will be negligible. Hence we can have an idea of the comparative particle size of these from the values of their relaxation times. From this, therefore, it may be seen that the ultimate rotating particles of pure lac resin and soft lac resin are practically equal in size. Dammar rotators are bigger in size than lac particles, whilst mastic resin has a still bigger rotating unit. This finding is in conformity with our previous results where we have seen that the radii of rotators of pure lac, soft lac, dammar, and mastic are 1·5 Å, 1·5 Å, 2·7 Å and 4·4 Å respectively. Too much stress cannot of course be laid on the absolute value of any relaxation time obtained experimentally from measurement on dilute solutions of these resins since it may be considered that the change in dielectric constant is only a second order effect and so the calculated value will have considerable accumulated errors. But as the accuracy of dielectric constant measurement is fairly high here (the accuracy ordinarily available for such measurements is very high now-a-days), their comparative values may safely be accepted. Gross, Ott and Arnold (1939) have similarly made use of this procedure in order to obtain the relaxation times of some methacrylate resins. The results obtained here are interesting and in agreement with the portions of curves obtained experimentally and showing anomalous dispersion (figure 1). Unfortunately the complete curves could not be obtained at present for reasons already stated. These results indicate, however, that we were on the right track in our previous calculations of particle size from dielectric loss and viscosity data.

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